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HYDROGEN ENTRY AND TRANSPORT MECHANISMS IN STRUCTURAL METALS.(U)

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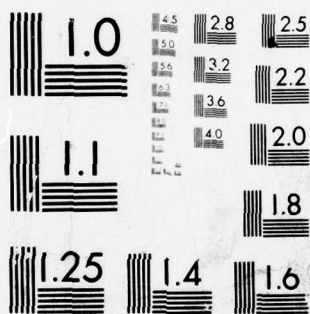
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FINAL TECHNICAL REPORT

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NOVEMBER 1979

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DEPARTMENT OF OCEAN ENGINEERING
UNIVERSITY OF RHODE ISLAND
KINGSTON, RHODE ISLAND

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20. Abstract (cont.)

- 1. Hydrogen permeation fluxes through iron membranes have been demonstrated to be affected by the reactivity of the membrane surfaces. The use of electroplated palladium entry and exit surfaces is recommended if the object of the study is to measure hydrogen mass transfer rates through a ferrous, or similar metal, membrane.
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3. Diffusivities based on times to reach steady-state could not be calculated for electrochemically-charged membranes because steady-state fluxes were never reached during the one-week duration of the permeation experiments.
4. An attempted determination of the effects of electroslag remelting on the hydrogen permeability of high strength steels could measure no significant difference between the steels tested. ←

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INTRODUCTION

Hydrogen Permeation:

The low temperature permeation of hydrogen through steel and other materials has been a subject of broad interest since the phenomenon was first reported in 1863 (1). The phenomenon has been known and studied for more than 100 years, but the mechanism(s) of hydrogen entry and transport in metals remain controversial and subject to continuing research and discussion (2).

While the subject is of considerable theoretical interest, it also has important practical aspects. Hydrogen embrittlement and stress corrosion cracking are serious engineering problems, and hydrogen permeation is an important aspect of these phenomena (3-8).

Table 1 is a summary of some data on low-temperature hydrogen permeation rates which have appeared in the literature. From this it is obvious that a wide variation in data exists, and a given researcher cannot compare his results with those obtained in another laboratory with any degree of certainty. This problem has been discussed at length by several authors. The variation in data can be attributed to a number of causes, some of which have been generally recognized (9-10), and some of which have not. These include:

1. Variations in calculation technique. This is a matter of continuing controversy and no generally-accepted means of calculating hydrogen permeation rates now exists (11-14).
2. Variations in hydrogen flux level. Hydrogen permeation is concentration dependent, and differences in inlet sur-

face hydrogen flux can be demonstrated to drastically alter the hydrogen permeation rate in ferrous alloys and other materials (15-16).

3. Variation in inlet-surface reactions. The effects of differences in inlet surface preparation procedures, to include cleaning method, surface roughness and coatings on sample surfaces have all been mentioned as reasons for alterations in hydrogen permeation behavior (10,13, 15).

Two general methods of measuring hydrogen permeation have been widely reported. Both involve introduction of hydrogen into one side of a metal membrane and measuring the rate at which it arrives at the opposite side of the membrane. Introduction of hydrogen into a metal from a gaseous phase has the advantage of easy control of relative inlet fluxes (16), and it has been widely used in the study of elevated temperature hydrogen permeation in metals. However, this technique is limited to relatively low fluxes, and it cannot duplicate the high hydrogen flux levels of interest in low temperature stress corrosion and hydrogen embrittlement studies (10). Electrolytic generation of hydrogen at cathodic metal surfaces can produce higher hydrogen concentrations in metal membranes and is the other common source of hydrogen for permeation experiments.

The hydrogen which permeates a membrane can be measured using gas pressure devices (19), mass spectrometers (20) or, more recently, using a potentiostatic technique (19,21).

Analysis of hydrogen permeation data reveals a number of problems inherent in all permeation experiments. Variations in

surface entry kinetics can greatly alter the measured flux rates. In 1941 Barrer (19) cited a lack of understanding of surface entry parameters as a major problem, and this problem has persisted to the present (13,17).

Some methods exist for separating surface effects from mass transport effects (e.g., comparison of the effects of membrane thickness on permeation rate) (13), but this remains one of the more important problems related to analyzing all types of permeation data (9). Solubility effects can affect mass transport through membranes of all types (19,22). Alterations in hydrogen trap densities, due to the interaction of the permeating hydrogen with the sample membrane, can be expected to occur during permeation experiments, and thus the effective "solubility" of hydrogen in a sample will change during the course of a permeation experiment. The substantial differences in hydrogen concentration between a sample inlet surface (high concentration) and the exit surface (normally assumed to be near zero) mean that concentration-dependent differences in hydrogen-membrane interactions will not be uniform throughout any given sample.

One method of overcoming differences in hydrogen entry kinetics and in concentration-dependent hydrogen-membrane interactions has been to use the same sample for a number of experiments, and to obtain "replicate" results by performing the same experiment on a sample after a number of charging and outgassing cycles have been performed and the sample has reached a "constant" permeability (13,23-24). This approach is of questionable merit if the purpose of a study is to evaluate the initial reaction of a metal with a

hydrogen-containing environment, such as might be the case if stress corrosion or hydrogen embrittlement were being studied. It may have justification for studying the diffusion, as opposed to trapping, aspects of permeation.

Problems in obtaining reproduceable hydrogen fluxes from sample to sample have also led to the practice of comparing relative fluxes, i.e. the flux at a given time in an experiment is expressed as a fraction of the steady-state flux obtained after a longer period of time. This "normalized flux" allows comparisons which cannot be made from direct measurements of hydrogen fluxes which may reach widely varying steady states (23).

A recent Cornell University report mentions the lack of apparent steady state fluxes in hydrogen permeation experiments involving electrochemically-generated hydrogen permeation in iron membranes (13). This confirms previously reported results at the University of Rhode Island (10,25-26).

The Electrochemical Hydrogen Permeation Technique:

The electrochemical hydrogen permeation technique was first introduced by Devanathan and Stachurski (21) and later refined by Bockris, Nanis, and coworkers at the University of Pennsylvania. It has the advantages of simplicity, low cost of the equipment involved, and the possibility for measuring the effects of widely varying hydrogen inlet fluxes on the permeation rates of hydrogen through metals. Unfortunately, the method has not been uniformly applied, and many organizations have encountered difficulties in employing this supposedly simple technique (10). Variations in the data reported using this technique can be ascribed to all of the reasons discussed previously. Nonetheless, this technique

has great promise and, with proper development, could produce the type of reproduceable data which has been unavailable up to now. The need for such data has been well documented and discussed (3, 10). One side of the sample (the right, or exit, side in Figure 1) is exposed to an aqueous solution and maintained at a constant anodic potential by means of a potentiostat. The current necessary to hold this sample at the preset potential is allowed to equilibrate to a minimum current value. Once a steady state background level is reached (less than 1 microamp/cm²), hydrogen is introduced into the opposite side of the sample by means of electrolysis or by gas-phase charging (21). The atomic hydrogen which passes through the sample and reaches the exit surface is immediately oxidized to hydrogen ions by the potentiostatic circuit. The change in current necessary to maintain the exit surface at the preset potential is a measure of the flow of hydrogen to the exit surface. Immediate oxidation of all atomic hydrogen reaching the exit surface maintains the hydrogen content at (or near) the surface very close to zero. Measurements of the time to achieve measurable flux at the exit surface, the shape of the permeation buildup curve (measured current, or calculated flux, versus time), and the total steady state flux then can be related to sample thickness, experimental temperature, and a wide number of other variables (10).

The apparatus shown in Figure 1 can be adapted for gas-phase charging by substituting a hydrogen-containing gaseous environment for the left-hand, or inlet, cell. The exit side of the apparatus remains the same.

PURPOSE

The final report on a previous contract (26) summarized the advantages of the electrochemical permeation cell shown in Figure 2 over the cell shown in Figure 1, which is typical of those in use at other universities. The additional research necessary to develop the electrochemical hydrogen permeation technique included the following objectives:

1. Development of a method to reproducibly charge the same amounts of hydrogen into the inlet surfaces of replicate permeation samples.
2. Determination of whether or not the lack of long-term steady-state hydrogen permeation fluxes, reported in Reference 25, was a real phenomenon, which had not been reported by other laboratories, or was the result of some experimental artifact which had not been identified.
3. Comparison of the effects of metallurgical variables on hydrogen permeation.

EXPERIMENTAL PROCEDURE

The permeation cell shown in Figure 2 was used for all electrochemically-generated hydrogen charging experiments undertaken in this study. The glass cell shown in Figure 3 was adapted for gas-phase charging experiments, but the right-hand, or exit, side of the experimental apparatus was maintained as shown. Details of both of these configurations are contained in a previous report (25).

The electrolyte used in all electrochemical cells was 0.2 N NaOH. This caustic solution is similar to the electrolytes reported in other laboratories (15,22,27-28,30,33-35). Other organizations have reported the use of sulfuric acid electrolytes (15,36-38), but the possibility of pH shifts seemed to dictate against the use of acid electrolytes, especially in the inlet cells where current densities would be higher (25). A recent report from MIT discusses experimental evidence to support substantial pH shifts at cathodically-charged electrode surfaces (15).

The introduction to this report mentioned problems with reproduceability of hydrogen fluxes between supposedly replicate samples of iron. Changes in permeation rates could be due to unidentified differences in surface preparation or experimental exposure. The other possibility is that the "permeability" of the iron samples was not identical. Preliminary efforts in this laboratory utilized replicate permeation samples removed from a single large sheet of Armco iron -- the most commonly reported permeation membrane material. An earlier report from the University of Rhode Island (26) indicated that satisfactory reproduceability between replicate samples had been obtained using Armco iron. Subsequent experiments indicated that Ferrovac E iron would have better reproduceability, and this is the substrate which has been used for all final results in this report and in the one earlier report on this contract (25).

RESULTS AND DISCUSSION

Reactivity of Entry and Exit Surfaces:

Any permeation membrane has, as a minimum, three types of reactions: surface reactions at the inlet surface, mass transport through the membrane, and surface reactions at the exit surface. In order to study the effects of metallurgical or environmental variables on any one of these sets of reactions means must be found to keep the other reactions constant, or changing in a known manner.

Exposure of the exit side of an iron permeation membrane to an electrolyte, such as NaOH, will cause the formation of a passive film of some sort under most conditions of potential and pH. The alternative to this is the occurrence of active corrosion, the formation of metal-containing ions as products of reaction between the metal and its environment. Obviously, either type of reaction could lead to altered, or uncontrolled, exit surface hydrogen reaction kinetics.

Similar reactions, and resultant changes in hydrogen charging efficiencies, can occur on hydrogen inlet surfaces.

The possibility of surface reactions between an iron membrane and its environment has led to the practice of plating the entry and/or exit surfaces with a supposedly nonreactive metal which would prevent reactions between the environment and the substrate. Palladium is commonly chosen for this purpose. An earlier publication details early experiments performed at the University of Rhode Island which were aimed at evaluating the effects of various palladium-coating techniques on measured hydro-

gen permeation fluxes (10). Figure 3 is reproduced from this report and shows that hydrogen permeation curves, while maintaining the same general shape, are definitely influenced by the presence of palladium coatings, as well as by their application method. Examination of sample surfaces, both before and after permeation experiments, led to the conclusion that the better (i.e. thicker with fewer cracks or holidays) the palladium coating, the higher the measured hydrogen permeation flux.

Subsequent work led to the adoption of electroplated-palladium surfaces for all permeation samples. The electroplated surfaces yield higher fluxes than those shown in Figure 3, and subsequent examination of the inlet and exit surfaces using the scanning electron microscope revealed a lower incidence of coating defects than were noted on surfaces that were palladium-coated using other techniques (39).

If the purpose of a hydrogen permeation experiment is to study the mass transport of hydrogen through the metal membrane, then the following criteria must be met for coatings on entry and exit surfaces.

1. The surface/environment interface must not become altered during the course of the experiment. Ideally the surface would not corrode during the course of the experiment, because corrosion could yield altered entry kinetics due to the replacement of an initial metal/environment interface with a combination metallic-corrosion product surface in contact with the environment. The hydrogen reaction kinetics on metal oxides are to be expected to be different from those of the original

metal, and experimental evidence is available to suggest that metal oxides are effective hydrogen permeation barriers (40-43).

2. Reproduceable hydrogen entry kinetics must be maintained between various samples. This requirement is twofold. First, if mass transport is to be studied, a method must be available whereby the same flux can be introduced into samples having different mass transport characteristics. Variations in sample chemistry, heat treatment, or mechanical loading have been postulated to alter hydrogen mass transport through metal permeation membranes. These same variations can also alter surface entry (or exit) reactions, and thus the need for separating the surface effects from mass transport effects is maintained. Additionally, a technique that insures reproduceability of permeation fluxes between replicate samples would allow the conclusion that changes in mass transport between samples having replicate entry and exit surfaces, but different substrates, could be ascribed to differences in mass transport through the substrate. Comparisons of this type have been the objective of several hydrogen permeation studies, but lack of control over surface conditions has made most of the reported conclusions questionable (45).
3. The coating should not be mass-transport rate controlling. This can be simply checked by changing the thickness of the entry and exit surface coatings. If the same per-

meation fluxes are noted, then the thickness, and thus the mass transport, of the surface coatings does not have a measureable effect on the measured hydrogen permeation flux.

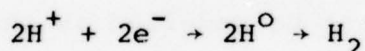
Figure 3 compares the hydrogen permeation fluxes obtained using different coating techniques. A comparison of the coating method used shows that higher fluxes were obtained with palladium coating methods which produced better coating-substrate bonding, fewer holidays, and less corrosion of the iron substrate. In other words, the better the palladium coating, the higher the hydrogen flux level. Figure 3 shows the results on Armco iron substrates. Subsequent work showed that electroplated palladium produced higher, more reproduceable flux levels. A concurrent change to Ferrovac E substrates, discussed below, prevents presentation of the electroplated-palladium data on Figure 3. Figure 4 compares permeation transients through Ferrovac E samples having electroplated palladium entry and exit surfaces versus no surface coatings.

The reproduceability of data using Ferrovac E samples is shown in Figure 5. The need for saturating samples or using normalized flux measurements to compare data between different samples has obviously been eliminated by choosing reproduceable entry kinetics (electroplated palladium entry surfaces) and reproduceable permeation membranes (Ferrovac E).

The question of whether or not palladium coatings alter the measured mass transfer rate of hydrogen through a palladium-iron-palladium membrane needs to be examined separately insofar as hydrogen entry and mass transfer are concerned. Figure 6 shows

hydrogen permeation transients through two Ferrovac E membranes, one of which had a palladium coating thickness twice that of the other. No measureable difference was obtained in experiments of this type at any flux level using either electrolytic or gas-phase charging. This led to the conclusion that the thickness of the palladium layer did not alter the mass transport properties of the palladium-iron-palladium membranes. Thus it could be assumed that any differences measured were due to the permeability characteristics of the iron membrane. A further test was to alter the thickness of the iron membrane and see whether or not the permeation results were consistent with the predicted relationship that steady state flux should vary linearly with inverse flux (23,25,47). Figure 7 shows results for three different gas-phase charging pressures which indicate that the flux levels were controlled by the sample thickness and not by surface effects or palladium-iron interface effects (25). Similar effects could not be determined for electrolytic charging due to the lack of a steady-state flux. This lack of a steady-state flux will be discussed in more detail later in this report. A recent paper by Early of the National Bureau of Standards (46) disputes the earlier claim by Namboodhiri and Nanis that hydrogen permeation is concentration dependent (15). Early reports steady-state exit surface fluxes on palladium membranes (measured as potentiostatic current) which are up to 94% of the entry surface cathodic charging current. This suggests that virtually all of the electrolytic hydrogen being generated on the inlet surface is being absorbed into the membranes and transported to the exit surface. A seemingly contrasting set of results was presented by

Chigirinskaja and coworkers who showed that the introduction of palladium ions into the cathodic cell of a permeation apparatus would lower the measured hydrogen permeation flux through an iron membrane, supposedly due to the inhibiting action of palladium metal ions which would be deposited on the iron surface (47). The seeming differences in results between those reported by Early and by Chigirinskaja, et al, may be due to differences in charging current density (1×10^{-6} amps/cm² for Early, 1×10^{-3} amps/cm² for the Russians). The results of Figures 3 would seem to contradict Chigirinskaja, et al, and be more in agreement with Early. The electrolytically-charged hydrogen permeation experiments conducted in this investigation tended to use charging current densities in the 1 amp/cm² range (26) similar to those reported by the Russians and several orders of magnitude higher than that reported by Early. Whether or not palladium increases or decreases the hydrogen recombination step of the reaction



seems to be still open to question, and the efficiency of the recombination reaction can obviously affect the amount of hydrogen available for mass transport in a manner similar, but perhaps opposite, to that postulated by Smialowski for hydrogen recombination poisons such as arsenic and cyanide (48).

Smialowski suggests that gas-phase hydrogen charging should be somewhat analogous to liquids, and those elements, ions, or compounds which tend to promote either hydrogen recombination or hydrogen entry are likely to behave in a roughly similar manner in both the liquid and gas states.

The fact that palladium can be expected to remain unreacted in many environments where iron would react can be shown by comparing Figures 8 and 9, the potential -pH Pourbaix diagrams (49) for iron and palladium. Figure 9 suggests that palladium hydrides may form under certain conditions. Extrapolation of Early's calculations (46) on this question to the current densities and sample thicknesses used in these experiments suggests that this may have occurred. Nonetheless the data shown in Figure 6 suggests that mass transport through the palladium iron-palladium membranes was not measurably affected by any palladium hydrides which may have formed.

The results of the investigations into surface reactivity and surface coatings may be summarized as follows:

1. Uncoated entry and exit surfaces were shown to react with all electrolytic and gaseous environments examined. This created time-dependent alterations in hydrogen entry reactions which could not be modelled as thus needed to be avoided.
2. Electroplated palladium entry surface produced identical hydrogen permeation fluxes when applied to replicate Ferrovac E iron substrates. These surfaces did not degrade over the course of permeation experiments of up to one week.
3. The presence of 2000 Å of electroplated palladium did not alter the hydrogen mass transfer rate through iron samples approximately $5 - 10 \times 10^{-2}$ cm thick.

Electrochemical Charging Experiments:

A previous University of Rhode Island report discusses the fact that, at that time, we had been unable to produce the steady-state hydrogen permeation fluxes reported in other laboratories. Extensive effort at this university resulted in modifications to the electrolytic cell design, membrane substrate identity, and surface coating procedures discussed above. Nonetheless, no reproduceable long term steady-state hydrogen permeation fluxes were achieved in any experiments on electrochemically-charged hydrogen permeation experiments on iron membranes. For this reason, a standard procedure was adopted whereby all electrolytic charging experiments were terminated after approximately one week (168 hours) of electrolytic charging.

Figure 10 shows an electrolytically-charged hydrogen permeation transient. The hydrogen flux is obviously still increasing after 100 hours. Thus the apparent diffusivity, which has commonly been calculated based on the time to reach a designated fraction of steady-state flux (10,23,25,47,50) cannot be determined from data which does not reach steady-state. An earlier University of Rhode Island report discusses wide discrepancies in data based on time to reach a stated portion of steady-state permeation fluxes (26). Recent reports by other organizations have acknowledged the lack of steady-state fluxes, at least on occasion, with electrochemical charging (13,22). Thus the data reviewed in this laboratory's previous report must be considered with renewed skepticism, and the possibility exists that any steady-state fluxes which have been reported must be considered to be, possibly, the result of a surface degradation, which would reduce

hydrogen entry efficiency, being balanced by a long-term tendency towards increasing fluxes.

The electrochemical hydrogen permeation technique must, of necessity, postdate the development of the potentiostat. Thus no hydrogen permeation data is available prior to Devanathan and Stachurski's 1962 report. Nonetheless, earlier experimental literature, reviewed by Barrer in 1941 (19) and updated by Davis and coworkers for steels in 1961 (51) would indicate support for substantially slower diffusivities at low temperatures than have frequently been reported using derivations of the Devanathan and Stachurski technique (26).

Early reviewed the literature available on hydrogen permeation in palladium and compared it with his data on permeability obtained using the electrolytic technique. He reported values of the order of $3 \times 10^{-7} \text{ cm}^2/\text{sec}$, in substantial agreement with the values of Devanathan and Stachurski. These compare with values for iron in the $10^{-5} \text{ cm}^2/\text{sec}$ range summarized in our earlier report (and repeated in Table 1) (26). It is interesting to note, however, that hydrogen is frequently purified by passing through palladium membranes. If the permeability of iron were, in truth, faster, it would seem that the cheaper material would be used for this purpose.

While a number of problems have been identified in trying to use electrochemically-charged hydrogen permeation membranes, this still appears to be the only available technique which can introduce the high hydrogen fluxes necessary to characterize hydrogen permeation associated with hydrogen embrittlement and stress corrosion cracking.

Comparison of Electrochemical and Gas-Phase Charging Experiments:

Results of the gas-phase charging experiments conducted in this laboratory have been discussed in detail in an earlier report (25) and will only be summarized here.

Comparison of the electrochemical charging data of Figure 3 with the gas-phase charging data of Figures 4 and 5 reveals that the time necessary to reach steady-state fluxes was substantially shorter for gas-phase charging experiments than it was for electrochemical charging. Initial experiments were run for periods of more than one week to check for the possibility of any long-term flux increases. None were noted in any gas-phase charging experiments conducted in this investigation.

The lack of a long-term increase in the gas-phase experiments, and its presence in the electrochemical experiments, may be due to a fundamental difference between the two techniques, which were intended to provide complementary data. What seems more likely is that the high hydrogen fluxes encountered in the electrochemical charging experiments caused greater changes in hydrogen trap densities, or occlusion rates (52), than were caused by the lower flux levels of the gas-phase experiments. The possibility exists that longer gas-phase charging experiments, achieving the same total integrated hydrogen flux through the permeation membrane, might have caused similar long-term increases in flux rates in gas-phase experiments. However, the possibility also exists that trap growth and diffusion-related permeation occur competitively and, at certain flux levels, the effect of one phenomenon would mask, and preclude the detection of, the other. This

type of situation has been demonstrated in the relatively long-term (100 hours and more) elevated-temperature steel outgassing experiments reported by Werner and Davis (51).

Other explanations involve the sensitivity of the instrumentation used in this experimentation. The cathodic current densities used in this investigation were chosen to replicate the range of current densities commonly reported in the literature summarized in Table 1. The practice of normalizing flux data (presenting reported fluxes as fractions of steady-state fluxes) prevented any logical prediction of the relative exit surface fluxes to be obtained using electrochemical charging and gas-phase charging. An attempt was made to accomplish an overlap in flux levels between the lowest fluxes achieved by electrochemical charging and the highest fluxes obtained by gas-phase charging. Figure 10 shows the electrochemical charging transient for the lowest current density employed in this research, approximately 3×10^{-6} amps/cm² after 100 hours. This is three times the highest steady-state flux achieved by gas-phase charging (25). Thus no direct comparison between charging rates at the same flux levels was possible based on the experimental results of this investigation.

A more important comparison between the data is that, even when steady-state permeation fluxes were achieved for gas-phase charging experiments, the times necessary in this research for the permeation curve to level off or reach steady-state are considerably longer than times reported elsewhere (23,32,35,53,54). The times to steady-state reported elsewhere range from 10 minutes

down to 1 minute (23,32,35,53,54). These researchers do not show the permeation transients for a long-term situation, say 10 hours. In this study a steady-state was reached in most cases in less than 5 hours, but in a few cases steady-state was not attained until 10 hours.

Thus in either case, electrochemical or gas-phase charging, the diffusivities obtained in this research, assuming the mathematical treatments of McKnabb and Foster (12) as adopted by Boes and Zuchner (50) are appropriate, yield slower diffusivities than most of those that have been reported elsewhere. In any case, the data indicates a slower, or perhaps in some cases nonexistent, achievement of steady-state flux levels. The reproducibility of the experiments in this investigation, as compared to those frequently reported elsewhere, leads us to believe that this slowly-achieved, or perhaps nonexistent, steady-state flux level is not an experimental artifact. Recent mention in print of the same phenomenon by other universities, at least for electrolytically-charged membranes, lends credence to this idea (13, 24).

METALLURGICAL STUDIES

The electrochemical hydrogen permeation technique has been used to study the effects of a number of metallurgical variables on hydrogen permeation.

An early attempt in this laboratory was to determine the effects of electroslog remelting on the hydrogen permeability, and thus the hydrogen susceptibility, of high strength steels.

The reluctant conclusion of this research was that the experimental sensitivity of the technique was not sufficient to detect the differences, if any, in the hydrogen trapping characteristics of the materials tested (45).

A review of attempts by other organizations to measure the effects of alloying variables on hydrogen transport reveals a common tendency to not separate the hydrogen entry phenomena, which can be markedly affected by alloying, from the mass transport effects, which remain to be proven. It is suggested that using a nondegrading, reproduceable surface coating, such as the 2000 Å thick electroplated palladium coatings used in this research, would allow unambiguous separation of mass transport effects from surface effects.

SUMMARY

The results of this research can be summarized as follows:

1. Hydrogen permeation fluxes through iron membranes have been demonstrated to be affected by the reactivity of the membrane surfaces. The use of electroplated palladium entry and exit surfaces is recommended if the object of the study is to measure hydrogen mass transfer rates through a ferrous, or similar metal, membrane.
2. The apparent hydrogen diffusivity rates determined in this research are slower than those commonly reported in the literature.
3. Diffusivities based on times to reach steady-state could not be calculated for electrochemically charged membranes

because steady-state fluxes were never reached during the one-week duration of the permeation experiments.

4. An attempted determination of the effects of electroslag remelting on the hydrogen permeability of high strength steels could measure no significant difference between the steels tested.

TABLE 1. LITERATURE VALUES OF HYDROGEN PERMEATION DATA FOR IRON AND STEEL (26)

SOURCE	YEAR	MATERIAL	TEMP (°C)	APPARENT DIFFUSIVITY ($\times 10^5 \text{ cm}^2 \text{ sec}^{-1}$)	CHARGING MEDIUM	INLET CONCENTRATION	CALCULATION METHOD
Nambodhiri and Nanis	1972	Armco Iron	22	2.14 - 3.48	NaOH	---	$t_{0.5}$
		Armco Iron	22	5.53 - 8.45	H_2SO_4	---	$t_{0.5}$
		4340	22	0.667 - 1.140	NaOH	---	$t_{0.5}$
		4340	22	1.71 - 2.19	H_2SO_4	---	$t_{0.5}$
Nambodhiri and Nanis	1970	Armco Iron 2% Cold Rolled	21	0.50	NaOH	---	$t_{0.5}$
Gileadi	1966	Armco Iron	27	2.0	NaOH	---	Unstated
		Fe-CR(10%)	27	0.002	NaOH	---	Unstated
Dillard	1972	Zone Refined Iron	24	7.0 - 7.8	H_2SO_4 with As_2O_3	---	$t_{0.63}$
Bockris and Devanathan	1962	Armco Iron	25 ± 2	8.3	Various	---	$t_{0.63}$
Beck, Bockris, Genshaw, and Subramanyan	1970	Armco Iron	27	5.0	NaOH	---	$t_{0.5}$
		Armco Iron	80	9.0	NaOH	---	$t_{0.5}$
Devanathan and Stachurski	1962	Armco Iron	24 ± 2	3.5 - 8.9	H_2SO_4 and NaOH	---	$t_{0.63}$
Wach, Miodownik, Mackowiak	1966	High Purity Iron	25	2.5	Gas Phase	---	t_0
Fontana and Wang	1972	4340	25	.01 - .032	0.2N NaOH	---	$t_{0.5}$
Beck, Bockris, McBreen, Nanis	1965	Zone Refined Iron	25 ± 1	6.05	NaOH	---	Unstated
		Armco Iron	25 ± 1	6.02	NaOH	---	Unstated
		Armco Iron Single Crystal	25 ± 1	8.25	NaOH	---	Unstated
		4340	25 ± 1	.00251	NaOH	---	Unstated
Kumnick and Johnson	1974	Armco Iron	25	1.3	NaOH or Gas Phase	Some Pd	$t_{0.63}$
Berman, Beck and DeLuccia	1974	4340	25	.025	NaOH + NaCN	---	$t_{0.83}$
Beck, Bockris, McBreen, and Nanis	1966	4340	Unstated	0.11	NaOH + NaCN	---	$t_{0.5}$
Kim and Loginow	1968	3Ni - 1.5 Cr 0.5 Mo Steel	25	0.063 - 0.3	NaOH	---	$t_{0.63}$
Berman	1974	HY 130	25	0.01 - 0.04	Unstated	---	Unstated

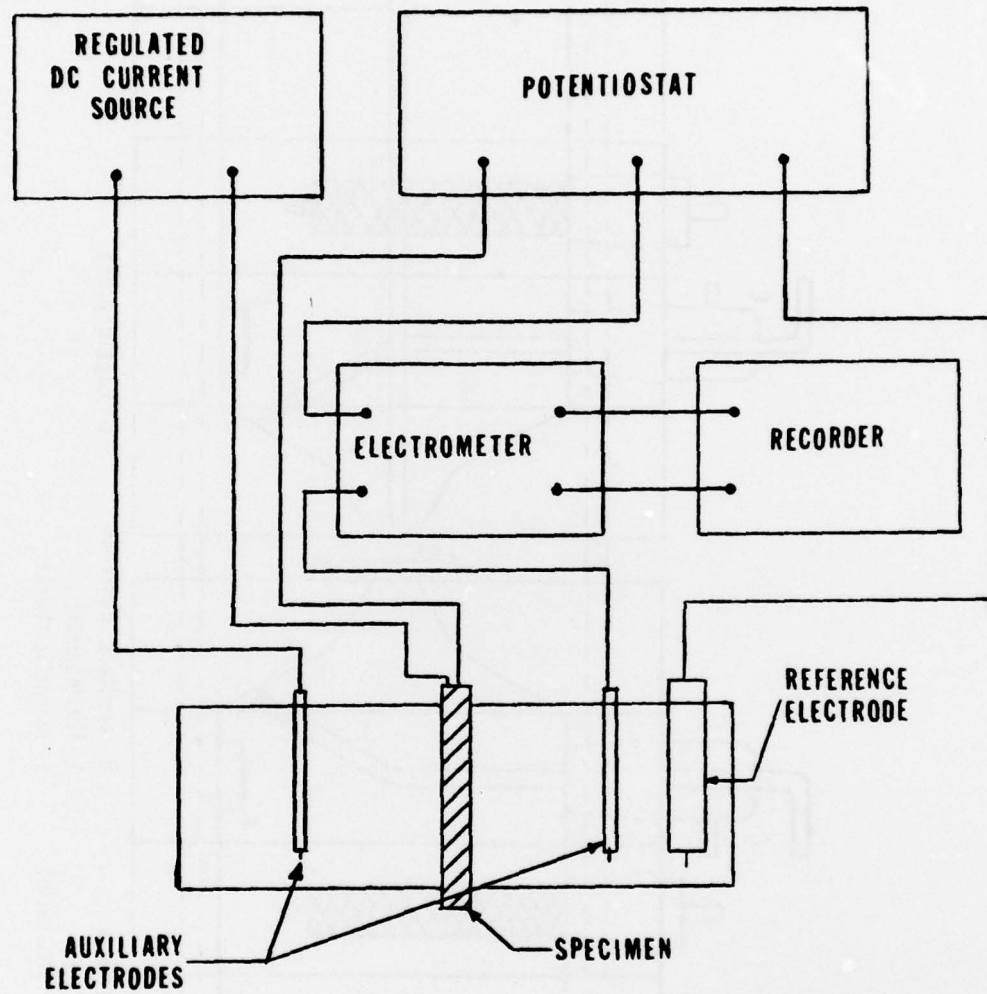


FIGURE 1. BLOCK DIAGRAM OF THE ELECTROCHEMICAL HYDROGEN PERMEATION APPARATUS USED IN THIS INVESTIGATION.

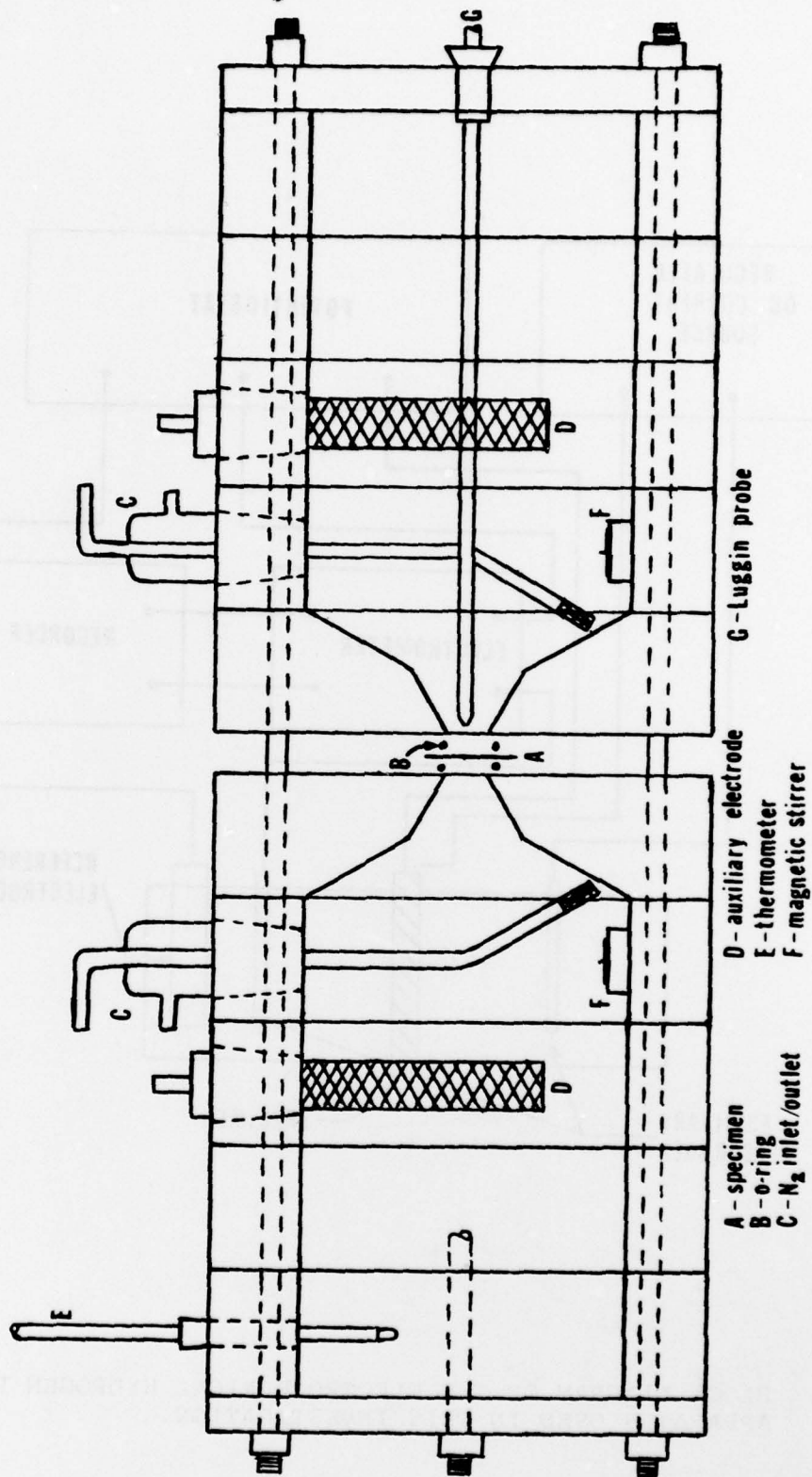


FIGURE 2. HYDROGEN PERMEATION CELL USED IN THIS INVESTIGATION.
 CONTAINER IS CONSTRUCTED OF TEFLON WITH PLEXIGLASS ENDS.

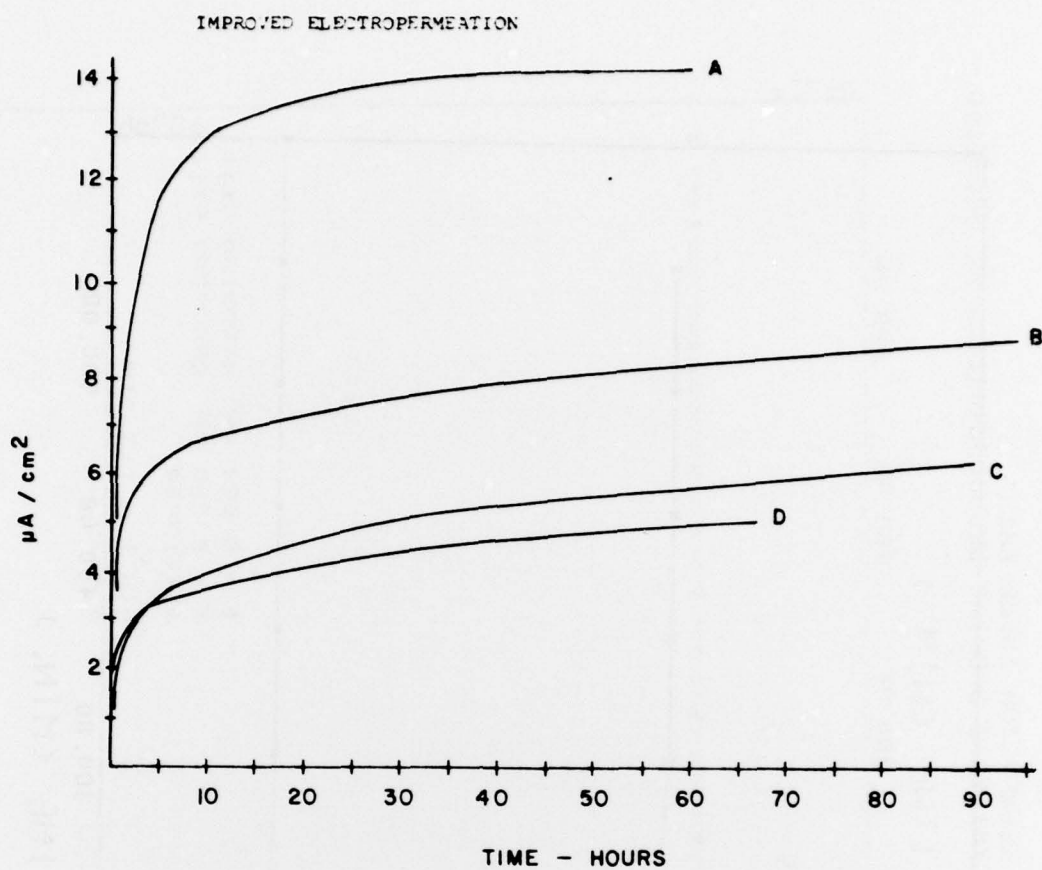


FIGURE 3. HYDROGEN PERMEATION TRANSIENTS FOR ARMCO IRON WITH DIFFERENT SURFACE PREPARATIONS: A = ION PLATED Pd, B = VAPOR DEPOSITED Pd, C = ELECTROLESS Pd, D = BARE IRON (10).

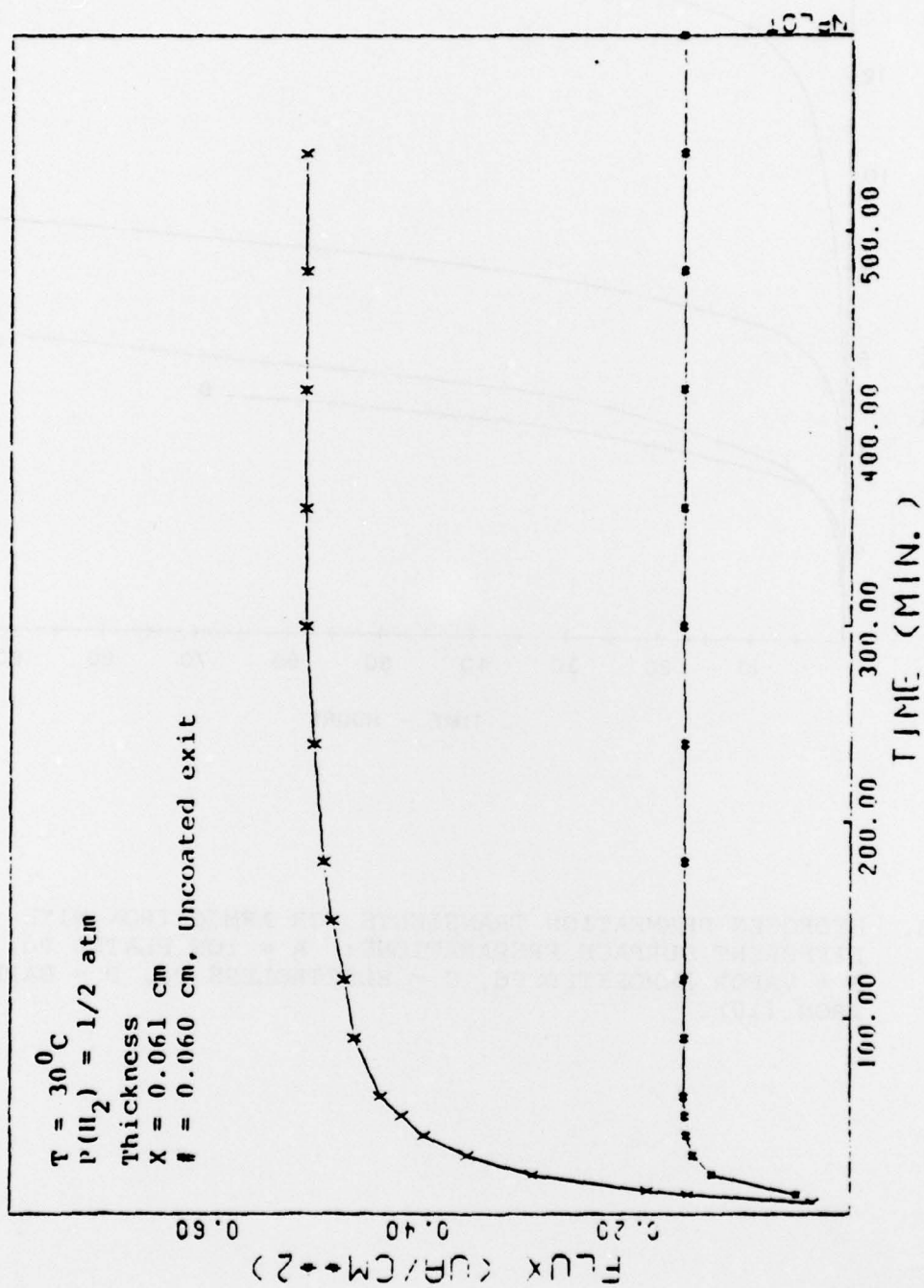


FIGURE 4. ABSORPTION TRANSIENTS COMPARING COATED AND UNCOATED SAMPLE MEMBRANES (25).

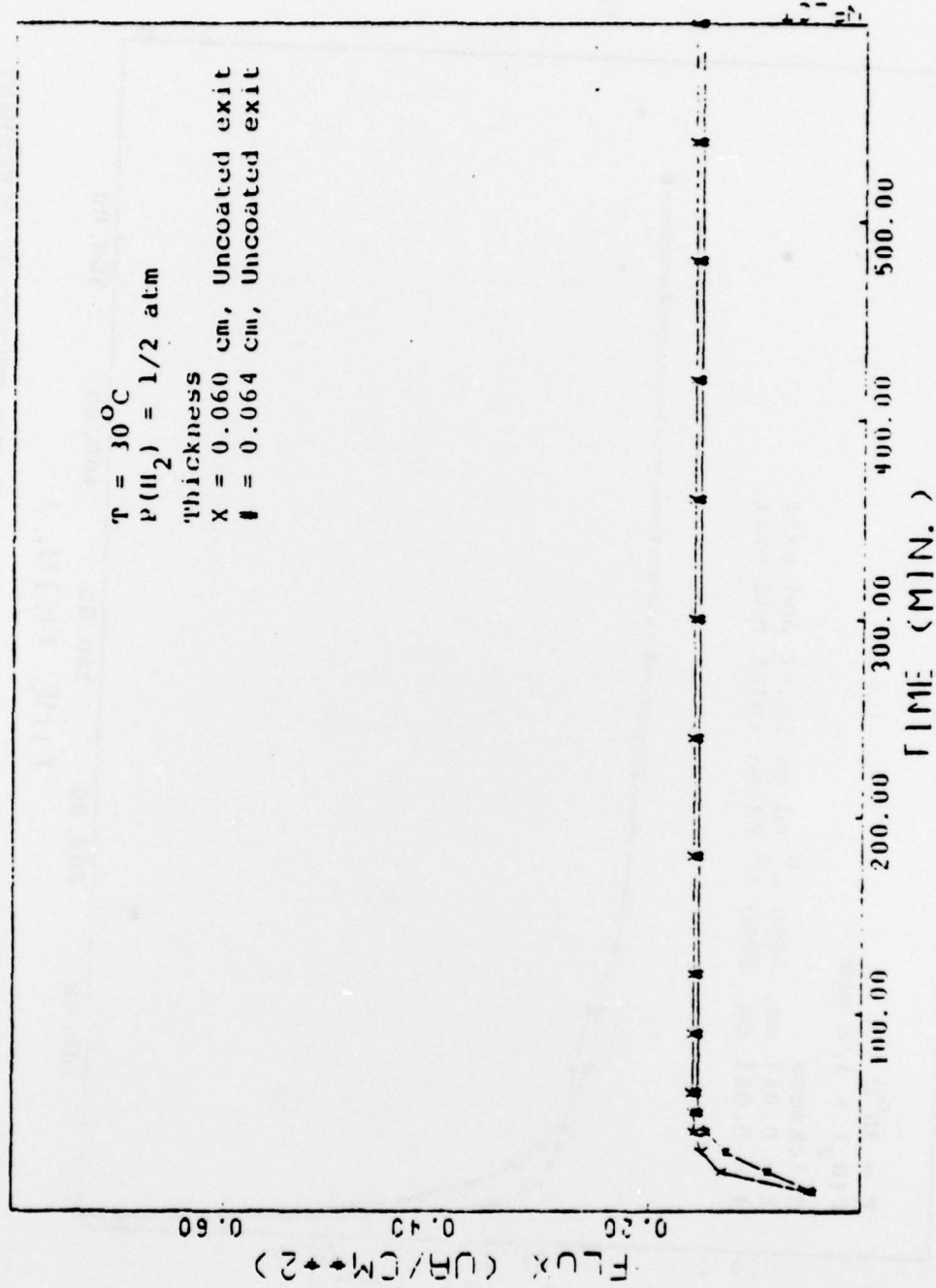


FIGURE 5. ABSORPTION TRANSIENTS SHOWING REPRODUCIBILITY OF UNCOATED EXIT SURFACE PERMEATION TRANSIENTS.

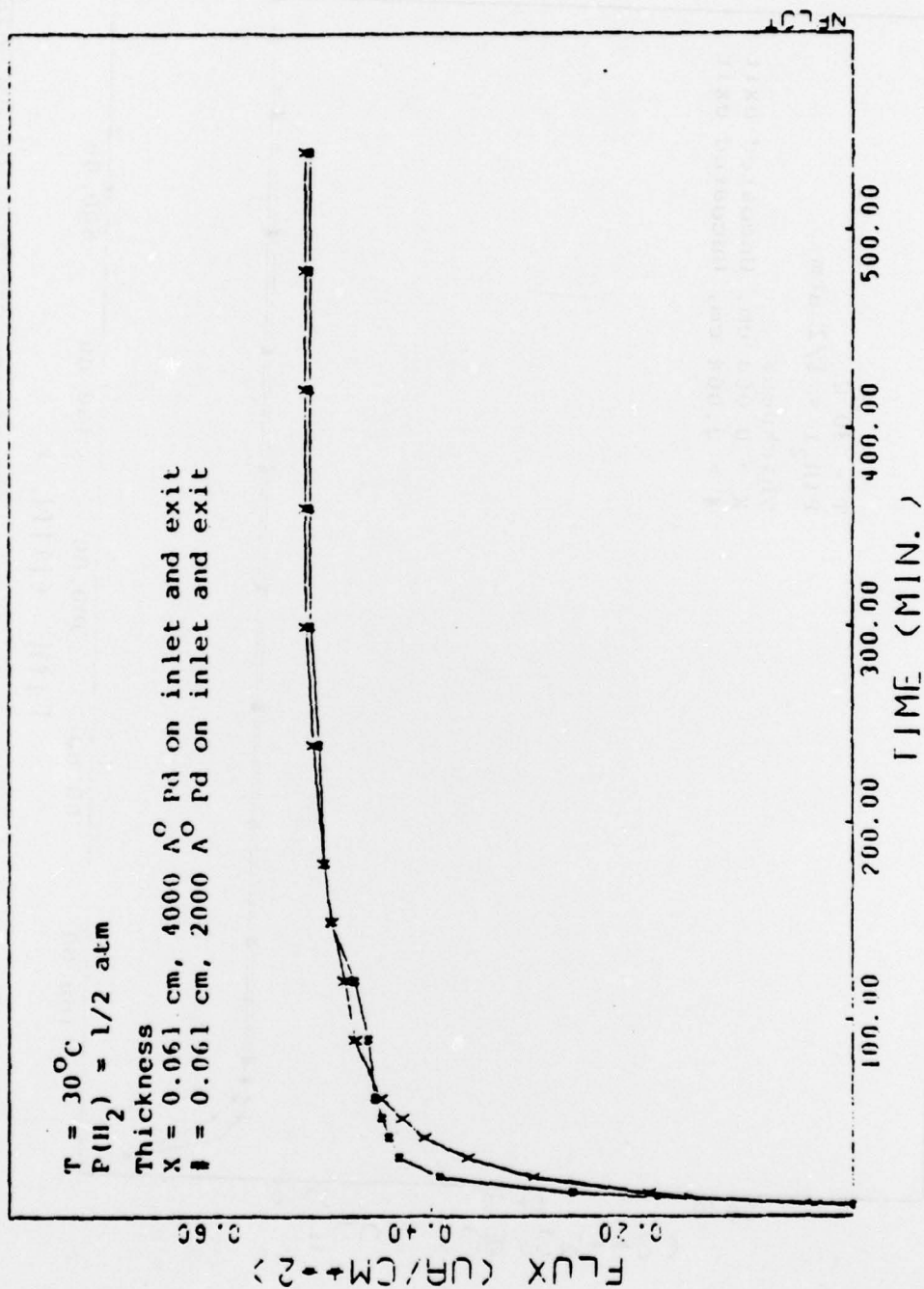


FIGURE 6. ABSORPTION TRANSIENTS SHOWING THE EFFECT OF DIFFERENT THICKNESSES OF PALLADIUM COATINGS (25).

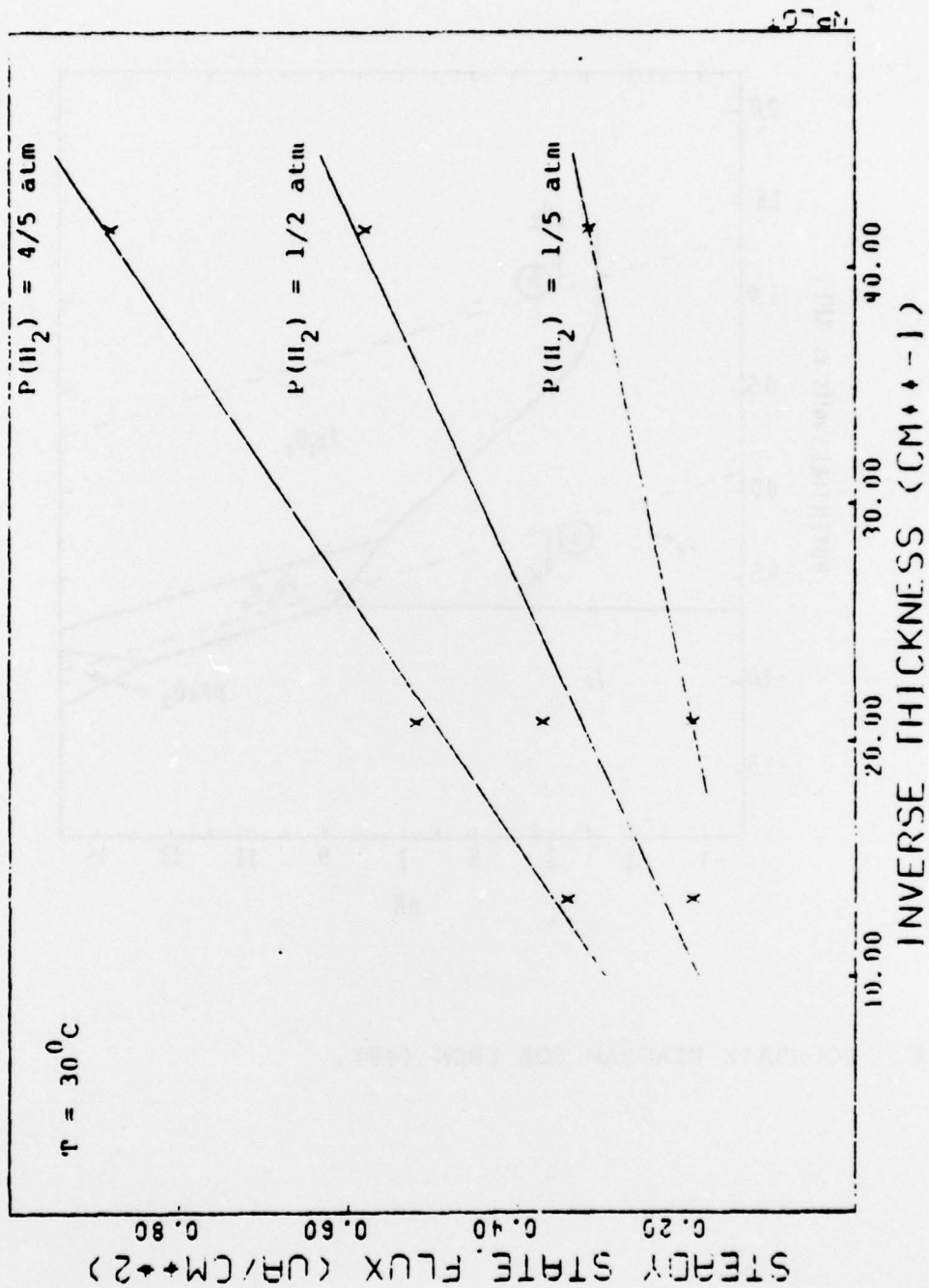


FIGURE 7. STEADY STATE FLUX AS A FUNCTION OF SAMPLE MEMBRANE THICKNESS (25).

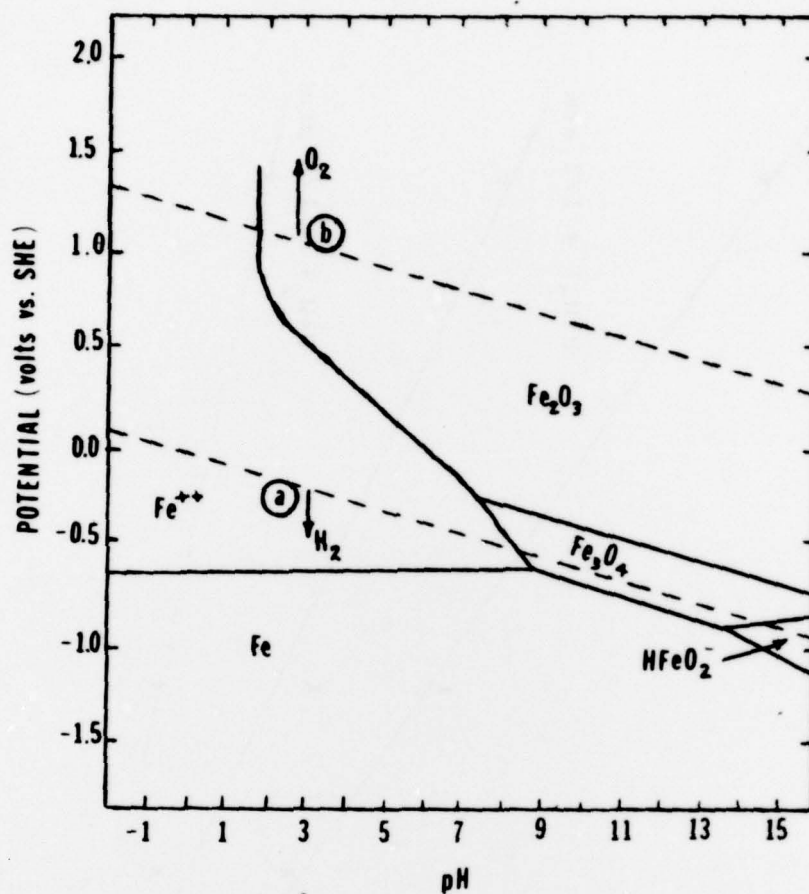


FIGURE 8. POURBAIX DIAGRAM FOR IRON (49).

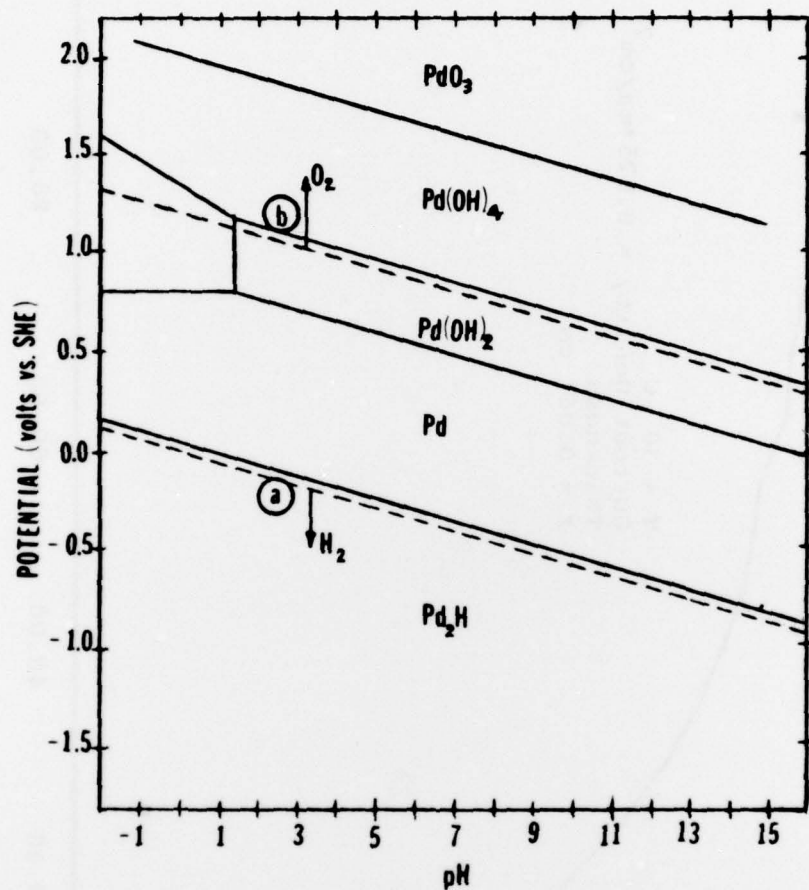


FIGURE 9. POURBAIX DIAGRAM FOR PALLADIUM (49).

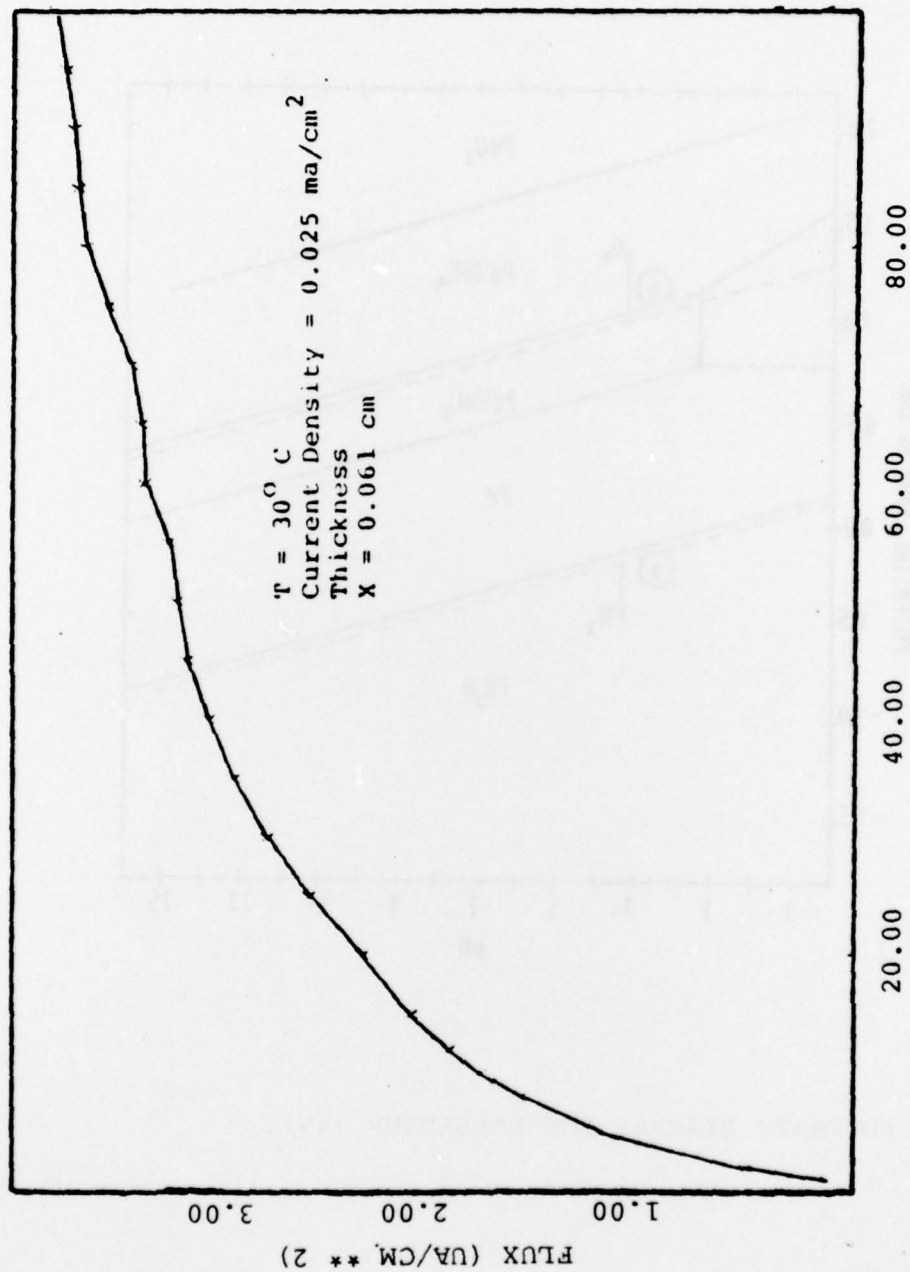


FIGURE 10. TYPICAL ELECTROCHEMICAL CHARGING TRANSIENT (25).

PUBLICATIONS SUPPORTED BY THIS CONTRACT

J. Jones, R. Heidersbach and M. Surkein, "Hydrogen Permeation of High Strength Steels", Paper Number 2801, Proceedings, Off-shore Technology Conference, Houston, May 1977.

R. Heidersbach and J. Jones, "Optimization of the Electrochemical Hydrogen Permeation Technique", Paper 4A3, Proceedings, Second International Conference on Hydrogen in Metal, Paris, June 1977.

M. Surkein, "Hydrogen Permeation in Iron at Low Temperatures", M.S. Thesis, University of Rhode Island, 1979. Issued on Interim Technical Report Number 1, March 1979.

PRESENTATIONS

"Hydrogen Permeation of High Strength Steels", Offshore Technology Conference, Houston, TX, May 1977.

"An Improved Electropermeation Technique for Studying Hydrogen Transport in Metals", Second International Conference on Hydrogen in Metals, Paris, June 1977.

"An Optimized Technique for Electrochemical Hydrogen Permeation in Ferrous Alloys", Electrochemical Society National Meeting, Seattle, WA, May 1978.

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